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Selective Removal of Sugars from Aqueous Solutions by Adsorption on Precipitated Iron(III) Hydroxide

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The removal of various mono-, di-, oligo-, and polysaccharides from aqueous solutions by adsorptive binding to precipitated iron(III) hydroxide was very selective in respect of their stereo-chemistry and chain length.

Hydrated Fe(III) ions are hydrolyzed at pH > 2.5 to form a precipitate of $Fe(OH)_3$,[1] while they do not in the presence of excess sugars.[2] This fact indicates that Fe(III) ions interact with sugars to form soluble complexes.[3] Mainly by magnetic susceptibility measurements in aqueous solutions, we have revealed that soluble complexes including $Fe(OH)_3$ or its analogue are formed in the Fe(III) ion solutions of excess sugars or sugar alcohols in the pH range 2.5 to 10, as well as in those of poly(vinyl alcohol) or water-soluble cellulose derivatives.[4,5] Now, there is very little doubt that cellulose and starch also interact with Fe(III) ions to form similar complexes.[5] All these facts suggest that the precipitate of Fe-$(OH)_3$ itself may be capable of interacting with sugars. The purpose of this paper is to investigate this interaction from the standpoint of the removal of sugars from aqueous solutions by adsorptive binding to precipitated $Fe(OH)_3$.

Various experimental conditions of the above removal of sugars have been tested, and the following condition has been adopted as a most reasonable one. Aqueous solutions of $FeCl_3$ and sugar were mixed in a volumetric flask at a concentration ratio of [monosaccharide unit]/[Fe(III) ion] of 0.20 on the condition of the final Fe(III) ion concentration of 100 mM. After the flask was allowed to stand overnight at room temperature, the optical rotation of the supernatant was measured with a JASCO DIP-370 degital polarimeter to determine the concentration of free sugar. For purposes of comparison, precipitated $Cu(OH)_2$ was also used as another absorbent under the same condition. All the sugars used here are listed in Table 1. All of them except four oligo-sugars were of the highest grade and used as received. The four oligo-sugars, which were a gift from Sanwa Denpun Kogyo Co., were mixtures of the oligosaccharides G2, G3, G4, etc. synthesized by the enzymatic hydrolysis of starch, where Gn expresses an oligosaccharide consisting of n glucose units. The contents of Gn ($n \geqq 4$) in the oligo-sugars A, B, C, and D were 62.4, 74.1, 89.6, and 94.5%, respectively.

All the results obtained here are summarized in Table 1. Inspection of this table reveals the following marked features in the removability of sugars. First, the $Fe(OH)_3$ precipitate is much more effective in the removability than the $Cu(OH)_2$ one, but there is a rough parallelism between them. Second, the removability is very stereo-selective for the monosaccharides, although details of this selectivity are not known yet. Third, the disaccharides are low in the removability compared with the monosaccharides. Trehalose is especially low, suggesting that the hemiacetal structure may be of importance here. Finally, an oligo- or poly-saccharide is higher in the removability, as its chain length is longer. In short, all these facts revealed here by use of such a familiar iron compound as $Fe(OH)_3$ are of great interest in connection with the molecular recognition and separation of sugars.

Table 1. Removability (%)[a] of sugars from aqueous solutions by adsorption on precipitated Fe(III) and Cu(II) hydroxides

Sugar[b]	$Fe(OH)_3$	$Cu(OH)_2$
D-Glucose	18.8±0.7	0.5±0.2
D-Fructose	36.2±1.6	6.2±0.2
D-Mannose	38.2±2.2	4.6±1.4
D-Galactose	13.0±0.4	0.4±0.3
Maltose	16.0±2.8	1.7±0.3
Sucrose	11.7±0.7	3.3±0.8
D-Lactose	11.2±0.9	1.4±0.1
D-Trehalose	6.1±0.8	1.1±0.2
α-Cyclodextrin	19.7±0.8	5.9±0.3
β-Cyclodextrin	34.8±4.0	8.8±0.1
γ-Cyclodextrin	42.3±2.3	16.6±0.5
Oligo-sugar A	55.5±0.4	20.2±0.6
Oligo-sugar B	56.6±0.3	26.1±0.4
Oligo-sugar C	79.4±0.5	38.9±0.4
Oligo-sugar D	83.6±0.3	41.5±0.5
Dextran[c]	100	31.6±0.5

a) The average of three or four measurements. b) See text, as to the oligo-sugars. c) mol wt ≈ 60000.

References

1) C. M. Flynn, Jr., Chem. Rev., 84, 31 (1984). 2) P. J. Charley, B. Sarkar, C. F. Stitt, and P. Saltman, Biochim. Biophys. Acta, 69, 313(1963). 3) L. Nagy et al., Inorg. Chim. Acta, 124, 55 (1986). 4) H. Yokoi, Y. Mori, T. Mitani, and S. Kawata, Bull. Chem. Soc. Jpn., to be published. 5) H. Yokoi, "Kobunshi Sakutai (Macromolecular Complexes)," ed by E. Tsuchida, Japan Scientific Society Press, Tokyo (1991), p. 181.

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